Spotlight on Chlorine

by Pamela J. Sutherland
Senior Scientist, Process Safety and Risk Management
Battelle-Columbus

Several thousand different chemicals are used in chemical laboratories and process operations throughout the DOE complex. One of the most ubiquitous is chlorine. This article spotlights chlorine as a hazardous chemical whose manufacture, storage, and use is regulated by both the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA).

Chlorine is a dense, nonflammable, greenish-yellow gas with a bleach-like choking odor. It is corrosive, highly toxic, and severely irritating to all tissue. Exposure may cause skin burns, permanent eye damage, and collapse of the respiratory system.

Chlorine is also a strong oxidizer. It reacts with organic materials, active metals, reducing agents, and ammonia. It reacts with water to form corrosive, acidic solutions. Most combustibles will burn in chlorine to form irritating and toxic gases. Thus, chlorine should be stored in a cool, dry, well-ventilated location, preferably outside, and separate from combustible, organic, or easily oxidized materials. It should be isolated from acetylene, ammonia, hydrogen, hydrocarbons, ethers, and finely divided metals.

At ambient temperature and pressure, chlorine is a gas. However, it is usually shipped in steel cylinders, in tank cars, or in tank barges, as a liquified compressed gas. Cylinders of chlorine may vent rapidly or explode when heated.

Because chlorine is typically stored in one-ton cylinders, a release presents a serious hazard to workers, co-located workers, and the public. Release of chlorine stored as a liquified gas at temperatures above its boiling point (-34°C) results in a superheated liquid. A fraction of the liquid chlorine immediately flashes to vapor. The remaining liquid either is suspended in the air as liquid aerosol or forms a liquid pool on the ground.

Liquid chlorine that accumulates on the ground initially boils if the ground temperature exceeds -34°C. If enough chlorine is present on the ground, however, heat transfer at the pool-ground interface eventually leads to ground temperatures below the boiling point. From this point, vaporization of the liquid pool is dominated by evaporation or entrainment of the chlorine from the pool surface by the ambient air.

A chlorine release under these conditions initially results in a gas cloud that is heavier-than-air. This dense cloud poses a hazard to individuals in the near vicinity of the release. However, entrainment of air through the sides and top of the cloud eventually results in a ground-level, neutrally-buoyant vapor cloud.

Small releases of chlorine that might result, for example, from slow-leaking or improperly connected cylinder valves pose a significant hazard only if they occur in enclosed space with inadequate ventilation.

Hazard Profile for Chlorine

Chemical	Description	Hazards	OSHA PSM/ EPA RMP Threshold Quantities	Exposure Limits ACGIH/ NIOSH/OSHA (ppm, mg/m³)	ERPG-1/ ERPG-2/ ERPG-3	Properties	Incompatibilities and Reactivities	NFPA Rating N _H , N _F , N _R
Chlorine (Cl ₂) (CAS 7782-50-5)	Gas: Dense, greenish-yellow, gas at standard temperature and pressure. Odor is pungent and very irritating. Liquid: Clear amber liquid under pressure.	Highly toxic by inhalation. Irritating and corrosive. Affects skin, eyes, respiratory system. Nonflammable. Noncombustible, but supports combustion as an oxidizing agent. Corrosive. Strong oxidizer. ACGIH: Not classifiable as a carcinogen.	OSHA: 1500 lbs EPA: 2500 lbs	ACGIH: TWA 0.5 ppm 1.5 mg/m³ ACGIH: STEL 1 ppm 2.9 mg/m³ NIOSH: Ceiling 0.5 ppm 1.45 mg/m³ (15 min)	1 ppm/ 3 ppm/ 20 ppm	Gas: Density = 3.21g/l at 0°C (32°F) and 1 atm (air = 1.29). Slightly soluble in water. Strongly electronegative. Liquid: Boiling point = -34°C (-29°F). Freezing/melting point = -101°C (-150°F). One liter of liquid = 456.8 liters of gas at 0°C (32°F) and 1 atm. Slightly soluble in water. Soluble in chlorides and alcohols. Extremely strong oxidizing agent. Low electrical conductivity.	Reacts explosively and forms explosive compounds with acetylene, turpentine, ethers, ammonia, hydrocarbons, hydrogen, and powered metals. Reacts with organic materials, active metals, and reducing agents. Reacts with water to form corrosive, acidic solutions.	3, 0, 0

References

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Acronyms and Abbreviations

ACGIH - American Conference of Governmental Industrial Hygienists

AIHA - American Industrial Hygiene Association

atm - atmosphere

oC - degrees centigrade (Celsius)

Ceiling -The maximum allowable human exposure limit for an airborne substance (NIOSH/OSHA). The ceiling value should/must not be exceeded during any part of the workday.

CAS - Chemical Abstracts Service (registry number)

CFR - Code of Federal Regulations
EPA - Environmental Protection Agency

ERPG - Emergency Response Planning Guideline (AIHA), chemical concentration in air designed to assist in the development of emergency response strategies

ERPG-1 - The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor.

ERPG-2 - The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action.

ERPG-3 - The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-

threatening health effects.

∘F - degrees Fahrenheit grams per liter

lbs - pounds

mg/m³ - milligrams per cubic meter

min - minute

NFPA - National Fire Protection Association
N_H - NFPA 704, hazard rating for health
N_F - NFPA 704, hazard rating for fire
N_R - NFPA 704. hazard rating for reactivity

NIOSH - National Institute of Occupational Safety and Health

OSHA - Occupational Safety and Health Administration

PEL - Permissible exposure limit (OSHA), a time-weighted average (TWA) chemical concentration in air that must not be exceeded during any 8-hour work shift of a 40-

hour workweek

ppm - parts per million

PSM - Process safety management (OSHA), regulation that contains requirements for management of hazards associated with processes using highly hazardous

chemicals to prevent or minimize the consequences of chemical accidents, promulgated as 29 CFR 1910.119, "Process Safety Management of Highly Hazardous

Chemicals"

REL - Recommended exposure limit (NIOSH), a time-weighted average (TWA) chemical concentration in air for up to a 10-hour workday during a 40-hour workweek

RMP - Risk management program, (EPA), regulation to prevent accidental releases of regulated substances and reduce the severity of releases that occur, promulgated as

40 CFR Part 68, "Accidental Release Prevention Requirements: Risk Management Programs Under the Clean Air Act, Section 112(r)(7)"

STEL - Short-term exposure limit (NIOSH/OSHA), a 15-minute TWA chemical exposure concentration in air that should not be exceeded at any time during a workday

TQ - Threshold quantity, (OSHA/EPA), the amount of a listed substance necessary to be covered by either PSM (29 CFR 1910.119) or RMP (40 CFR Part 68)

TLV - Threshold limit value (ACGIH), occupational exposure limit recommended by the ACGIH

TWA - Time-weighted average, the most frequently used exposure guideline term, representing the average concentration over a workday